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Appln. Trans.
PATENT

212 705-5000
FACSIMILE 212 705-5020

UTILITY PATENT
APPLICATION
TRANSMITTAL

(Only for new nonprovisional
applications under 37 CFR 1.53(b))

Attorney Docket No. A32188 PCT USA

First Named Inventor Wolfgang Held

Express Mail Label No. EJ408622280us

Total Pages 22

February 18, 1999

BY EXPRESS MAIL - Label No. EJ408622280US

Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

Sir:

Enclosed herewith for filing is a patent application of Wolfgang Held entitled SPARK-IGNITED
INTERNAL COMBUSTION ENGINE OXIDE GAS ABSORBING ARRANGEMENT AND METHOD

which includes:

[X] Specification 12 Total Pages
[X] Claims 8 Total Pages
[X] Abstract 1 Total Pages
[X] Drawing(s) 1 Total Sheets
 formal
 X informal

[x] Combined Declaration and Power of Attorney 3 Total Pages
[x] Newly executed (original or copy)
[] Copy from a prior application
 (for continuation/divisional only - **must be filed to avoid surcharge for late filing**)

If a continuing application, check appropriate box:

[x] Continuation [] Divisional [] Continuation-In-Part (CIP)
of prior International application No. PCT/EP97/04306

[x] Amend the specification by inserting, before the first line, the following sentence:

"This is a [x] continuation [] divisional [] continuation-in-part
of copending International application No. PCT/EP97/04306 filed August 7, 1997."

Attorney Docket No. A32188 PCT USA

- ☐ An Assignment of the invention to __.
- ☐ is attached. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
- ☐ will follow.
- ☐ has been filed in the prior application
- ☐ Small Entity Statement(s)
- ☐ Small Entity Statement filed in prior application. Status still proper and desired.
- ☐ Information Disclosure Statement (IDS) PTO-1449
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Basic Fee							\$760
Total Claims	63	-20 = 43	x \$9 =	\$0		x \$18 =	\$774
Ind. Claims	2	-3 = 0	x \$39 =	\$0		x \$78 =	\$0
Multiple Dependent Claim			+ \$130 =	\$0		+\$260 =	\$260
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Attorney Docket No. A32188 PCT USA

Priority

- ☒ Priority of application Country Germany, Appln. No. 196 33 050.5 filed August 19, 1996 is claimed under 35 U.S.C. 119.
- ☒ Certified Copy of Priority Document(s) Country Germany, Appln No. 19633050.5, filed August 19, 1996.
- ☐ is/are attached ☒ will follow ☐ has been filed in the parent application S/N .
- ☒ The Commissioner is hereby authorized to charge payment of any additional filing fees required under 37 CFR 1.16, 1.17, and 1.21(h) associated with this communication or credit any overpayment to Deposit Account No. 02-4377. Two copies of this sheet are enclosed.

BAKER & BOTTS, L.L.P.

By 

Ronald B. Hildreth

PTO Registration No. 19,498

Enclosures

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TO ALL WHOM IT MAY CONCERN:

Be it known that I, Wolfgang Held, a citizen of Germany, residing at Wilhelmstraße 1, D-38448 Wolfsburg, Germany, have invented an improvement in

SPARK-IGNITED INTERNAL COMBUSTION ENGINE
OXIDE GAS ABSORBING ARRANGEMENT AND METHOD

of which the following is a

SPECIFICATION

REFERENCE TO RELATED APPLICATION

This application is a continuation of International Application No. PCT/EP97/04307, filed August 7, 1997.

BACKGROUND OF INVENTION

This invention relates to absorbing arrangements and methods for temporarily storing oxides of nitrogen and sulfur and removing such oxides from the exhaust gas from spark-ignited internal combustion engines.

5 As used herein, the term "absorb" includes the chemical process for storing gases such as, for example, by conversion of barium oxide to barium nitrate for storage of nitrogen oxide.

United States Patent No. 4,755,499 discloses an arrangement for the reversible storage of oxides of nitrogen and sulfur, for example from motor vehicle exhaust gases, in
10 which the absorber is regenerated by heating in a reducing atmosphere. In this arrangement, a reduction of the nitrogen oxides takes place at the same time.

A storage catalyst of that type for use in motor vehicles is described in more detail in United States Patent No. 5,402,641, in which high temperatures above 500°C are necessary to regenerate the absorber. Consequently, use of the storage catalyst is possible only for motor vehicles having a high exhaust gas temperature, in particular for motor vehicles with an Otto engine.

In this case, however, the possibility of use is limited since, under certain operating conditions of internal combustion engines, such as occur for example in city traffic, the acceleration phases cause a large emission of nitrogen oxide, but no long lasting high temperature condition such as is required to regenerate the absorber, especially with respect to oxides of sulfur, is attained.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a spark-ignited internal combustion engine arrangement and method for releasably absorbing oxides of sulfur and nitrogen in exhaust gases which overcomes disadvantages of the prior art.

Another object of the invention is to provide a spark-ignited internal combustion engine having an absorber for nitrogen oxides in exhaust gases and a corresponding method, suitable especially for use with fuel consumption-optimized engines such as direct injection Otto engines, in which regeneration of the absorber is possible even at low exhaust gas temperatures.

These and other objects of the invention are attained by providing a spark-ignited internal combustion engine arrangement having an absorber for absorbing oxide gases which includes an absorption layer for absorbing oxides of nitrogen and/or sulfur on a support member and a control unit for controlling the temperature of the absorption layer so that the layer can be heated to a temperature at which it is regenerated by desorbing the NO_x and/or SO_x even at very low exhaust gas temperatures such as occur for example in the case of direct injection engines.

According to the invention, the usual gas absorbing materials may be employed, for example as described in United States Patent No. 4,755,499, and also in United States Patents Nos. 5,402,641 and 5,362, 463. A common feature of all these storage materials is that they have an elevated absorption temperature, while a still higher regeneration

5 temperature is required especially for removing the oxides of sulfur. For most storage media of this kind, temperatures in the range from 150° to 700°C, in particular temperatures above 300°C, are required. Such temperatures commonly occur in motor vehicles with Otto engines, but are comparatively rare with Diesel engines and especially in internal combustion engines having direct fuel injection.

10 The preferred NO_x storage materials are distinguished in that, under conditions of net oxidation, *i.e.*, a stoichiometric excess of oxidizing agents, such as occurs in the exhaust gas during the operation, they will store nitrogen oxides and, upon a reduction of the excess of oxygen, may reduce them. For this purpose, the NO_x storage catalysts usually include a precious metal, in particular the usual precious metal coatings for

15 three-way catalysts. The NO_x-laden storage material is advantageously regenerated in a regenerating phase at $\lambda \leq 1$.

Ordinarily, various reactions take place successively or simultaneously on the NO_x storage catalyst, the most important reactions being: oxidation of the NO in the exhaust gas to NO₂, storage of the NO₂ as nitrate, decomposition of the nitrate, and

20 reduction of the re-formed NO₂ to nitrogen and oxygen.

As described above, the course of the reactions depends, among other things, not only on the temperature of the catalyst but also on the concentration of the reagents at the active region of the catalyst and the flow velocity of the gas.

According to the invention, it has now been found that, with various factors

25 capable of being combined with each other, it is possible also, at little cost, to optimize the known exhaust gas absorbers so that they may be employed for spark-ignited internal

combustion engines with direct injection. For this purpose, the wall thickness of the supporting member on which the absorption layer is applied preferably should be ≤ 160 microns, and desirably ≤ 140 microns and if a metal support is used, a wall thickness ≤ 50 microns, preferably ≤ 40 microns, and desirably ≤ 30 microns, and the absorber
5 should preferably be heated to a temperature above the temperature of the exhaust gas.

According to the invention, it has been found that, with the use of thin walled ceramic supports for the absorption layer, i.e. supporting members having a wall thickness ≤ 0.14 mm, not only is a more rapid temperature rise of the absorption layer possible, but also a thicker absorption layer may be used. This accomplishes two
10 objectives: in the first place, even short periods of high temperature operation can be utilized for regeneration since the storage layer temperature will be increased to the required temperature more quickly, and in the second place, by providing a thicker absorption layer, a higher oxide gas storage capacity can be achieved so that during operation of the internal combustion engine a longer period of time can elapse before the
15 storage layer must be regenerated. Consequently, despite the less frequent occurrence of temperature peaks in the exhaust gas of consumption-optimized internal combustion engines, no failure of the storage layer resulting from exceeding its storage saturation limit will occur.

According to the invention, absorbers having a support member made of metal
20 foil are especially suitable, and the metal foil may advantageously be connectable to an electric power source for resistance heating so that, even at low exhaust gas temperatures, the absorber can be brought to the necessary regenerating temperature by passing an electric current through the metal support. Furthermore, by using a metal support member, the gas passages which are coated with the absorption layer may be variously
25 shaped, so that, for example, a controlled turbulent flow vortex of the exhaust gas in the passages can be established.

With especial advantage, according to the invention, supports with a variety of passage segments may be used for the absorber where, for example, an intermediate region of the passages is modified to produce a turbulent flow. This can be done, for example, by varying the passage cross-section, or by a twisting or distortion of the passages. In this way, the support may be adapted in a controlled way for especially favorable reaction conditions along the flow passages. Another special feature of the support, beside a possible variation in number of passages in the flow direction and the provision of changes of cross section along the flow direction, is the segmentation of the support where, for example, one segment with an absorption layer is disposed near the engine outlet and another segment with an absorption layer is located somewhat farther away. Thus, even with the most variable operating conditions, good NO_x purification results can be obtained with fuel consumption-optimized engines.

According to the invention, it has been found that the oxide gas storage arrangement will have especially good absorption and desorption properties if the flow passages for the exhaust gas are distorted in an intermediate region to achieve a turbulent flow between an inlet region and an outlet region which do not have a distorted structure to produce turbulent flow. As a simple arrangement for generating such a turbulent flow, for example, a transition from a large to a small diameter in the passages is effective, but twisting of the entire support in an intermediate region will also serve to generate turbulence. The especially favorable properties resulting from such turbulent flow are presumably achieved by a division of the individual reaction steps required to reduce nitrogen oxides among the successive regions of the support, with a modified intermediate region affording better conditions for reaction than unmodified intermediate regions.

To produce especially good oxide gas conversions, the absorption layer has an enlarged surface area, that is, a total surface area that is substantially larger than the area

of the surface of the support member on which it is coated. For this purpose, the absorption layer provides a surface area to which the exhaust gas is exposed of at least 20 m²/g, and preferably at least 40 m²/g. Also, the absorption layer preferably has a pore volume of at least 0.2 cm³/g, and desirably at least 0.4 cm³/g, a bimodal pore size distribution with both micropores and macropores also being acceptable. This may be achieved for example by the choice of the size of the particles forming the absorber surface, in which mixtures or specified distributions of different particle sizes are also suitable.

An especially suitable absorption material is gamma-aluminum oxide containing one or more elements in the group consisting of alkali metals, alkaline-earth metals, rare earths and/or lanthanum. The presence of the elements copper and manganese is also suitable. The added elements are usually present as oxides, or else as carbonates or nitrates, the storage effects being achieved by formation of corresponding nitrates and sulfates, which are then converted back to oxides or carbonates under the appropriate reaction conditions. In this way, it is possible to absorb NO_x and/or SO_x from an exhaust gas containing at least 1 % oxygen.

As described above, the absorbed substances are desorbed from the storage catalyst layer by elevated temperatures and in a reducing atmosphere. For this purpose, it is desirable to determine the oxygen concentration in the exhaust gas so that the oxygen concentration, or a quantity having a known relationship to the oxygen concentration, can be utilized to control the process of absorption or desorption.

Since the temperature of the absorption layer, determined directly or indirectly, is also important the same consideration is also applicable to the temperature of the exhaust gas. Thus, the absorption layer temperature may for example be determined by measuring the temperature of the exhaust gas or of the support member. A determination

of temperature over the operating diagram of the internal combustion engine is also possible.

With the present invention, absorption layers having a thickness of at least 50 microns, preferably at least 70 microns, and desirably at least 90 microns, can be provided. These values are average layer thickness of a cross section and should extend over preferably at least 50% and desirably at least 80% of the total absorber. The foregoing absorption layer thickness values apply to layers on ceramic substrates. Half of those values apply to absorption layers provided on metal substrates. Such high layer thickness values permit a greater storage capacity compared to conventional absorbers, and consequently permit longer intervals between regeneration as described above.

According to the method of the invention, regeneration of the absorption layer is preferably carried out when the operating conditions of the internal combustion engine produce a correspondingly high temperature of the exhaust gas and hence of the absorption layer. Especially advantageous, however, is a method in which supplementary heating of the absorption layer is provided, preferably electrically. Other possible heating procedures include ignition control measures in Otto engines, variation of lambda, lowering of lambda below 1, and addition of secondary air to generate exothermia on an oxidation catalyst, and/or an exhaust ignition arrangement, as well as heating the catalyst with a burner. A segmented absorber in which the segments are heated according to the required reaction is especially advantageous. Thus, for example, only one absorber segment located in a downstream exhaust flow direction may be heated, especially in case of a distinct spatial separation of the absorber segments. Electric heating is especially advantageous in this case, but an injection of fuel into the exhaust gas and/or a burner may also be used. By arranging individual segments for individual reactions at different distances from the engine exhaust manifold, thermal aging of the absorber may be

reduced in addition to providing the advantage of especially favorable reaction temperatures in individual absorber segments.

Since the release and conversion of the NO_x from the storage layer and the release of the oxides of sulfur from the storage layer require different temperatures, higher in the case of the sulfur oxides, it is also possible to proceed so that a desorption of the oxides of sulfur, which are present in particular as sulfate is performed at longer time intervals or only as needed, so that the storage layer is only occasionally heated to the high temperatures needed for desorption of the sulfur oxides. This counteracts premature aging of the storage layer, so that an especially good long term stability of the absorber is achieved. This procedure may be used with the absorber arrangement and method described above.

BRIEF DESCRIPTION OF THE DRAWING

Further objects and advantages of the invention will be apparent from a reading of the following description in conjunction with the accompanying single drawing illustration which shows schematically a representative embodiment of a spark-ignited internal combustion engine having an exhaust gas absorbing arrangement according to the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the typical embodiment of the invention shown in the drawing an absorber 1 of oxide gas components is mounted in an exhaust line 2 of an Otto-type internal combustion engine 3 the operation of which is controlled by a motor control unit 4. The motor control unit 4 controls an injection pump 5 delivering fuel from a tank 6 (not shown) to a fuel injection nozzle 7. In addition, the motor control unit 4 controls ignition of the fuel-air mixture in each engine cylinder by a spark plug 18. For the sake of clarity, the numerous conventional control lines for fuel and air supply and discharge and the like leading to the motor control unit 4 are not shown.

In the illustrated exhaust line 2 a three-way catalyst 8 is mounted downstream from the absorber 1 but it is also possible to locate the three-way catalyst 8 upstream from the absorber 1.

5 In this embodiment, the absorber 1 is made from two metal foils one of which is smooth and the other of which is corrugated and is connected to the smooth foil by soldering at the corrugation crests. By rolling this multilayer foil together, a cylindrical member having a plurality of coaxial passages is provided. In addition, the support member of the absorber has an intermediate region 15 which is twisted about its longitudinal axis, so that the individual passages 16 in the intermediate region are
10 narrowed and contorted to produce turbulence in the exhaust gases flowing through the passages. A similar turbulence generating structure in the intermediate region may also be achieved by providing transverse corrugations in one or both of the metal foils.

The metal foil material contains a few percent of aluminum and is anodized so that a "wash coat" containing gamma-aluminum oxide will adhere better to the metal foil
15 surface. The aluminum oxide wash coat further contains one or more of the elements sodium, barium, cerium and lanthanum, providing a layer on the aluminum oxide containing the salts, *i.e.*, nitrates, oxides and hydroxides of those elements. By impregnating the wound support foils with the wash coats and then firing, the absorbing layer with those salts is produced. Additionally, the absorbing layer is impregnated with
20 a solution containing salts of the precious metals platinum and rhodium and possibly palladium in addition to or instead of the rhodium, from which the corresponding precious metals are then liberated during firing. The resulting precious metal coating provides a three-way catalyst. The oxide gas absorber is provided with an electrical contact 9 and mounted in a housing so that an electric current can be passed through the
25 foils and the absorbing layer to a grounded housing. The electrical contact 9 is connected

to the control unit 4, and a temperature sensor 10, also connected to the control unit 4, is mounted inside the housing.

Upstream from the absorber 1, a broad-band lambda probe 11 inserted in the exhaust gas pipe, provides signals which are proportional to the oxygen concentration present in the exhaust gas to the control unit 4. In addition, a fuel injector 12 is mounted upstream from the lambda probe 11 and is supplied with fuel on instructions from the control unit 4. Between the absorber 1 and the following catalyst 8, an air injector 13 is provided, receiving air from a pump 14 controlled by the control unit 4.

The internal combustion engine 3 is an Otto-type engine with direct injection, producing exhaust gas which normally has a large excess of oxygen and a temperature of about 200° to 500°C. In operation of the internal combustion engine, nitrogen oxides and oxides of sulfur present in the exhaust are absorbed by the absorption layer of the absorber 1 in the form of nitrates and sulfates of sodium, barium, lanthanum and the like, while at the same time any oxidizable constituents present, mostly hydrocarbons, are oxidized by the precious metal coating of the absorber 1.

When the saturation limit of the absorbing layer in the absorber 1 is reached, or else at predetermined time intervals or in response to other control parameters, such as for example a determination of NO_x in the exhaust following the absorber, the absorber is regenerated, i.e. freed from the NO_x, incorporated for example as barium nitrate. At the same time, oxides of sulfur, incorporated for example as barium sulfate, may be removed as well. For this purpose, the control unit 4 determines by way of the temperature sensor 10 whether the temperature of the absorber coating is high enough for regeneration of the absorber layer.

If the absorber coating temperature is below 500°C, the fuel injector 12 injects fuel into the exhaust, which is catalytically burned with the oxygen present in the exhaust gas on the precious metal coating of the absorber 1, raising its temperature. Alternatively

and/or additionally, the metallic support for the absorber 1 can be electrically heated by a flow of current through the terminal 9. Still other arrangements for increasing the absorber temperature, as for example inductive heating of the metallic support and/or a throttling of the exhaust are possible.

5 As soon as the absorber 1 is heated sufficiently, a rich mixture is set in the exhaust gas, i.e. by the fuel injector 12 and/or a rich mixture as injected into the cylinder.

Preferably a throttle 17 is adjusted in the intake duct 16 of the combustion engine 3 by the control unit 4 so that less air is supplied to the internal combustion engine 3. This decreases the proportion of oxygen in the exhaust gas so that NO_x and SO_x are released
10 from the absorption layer and are reduced. Termination of the regeneration may be time controlled or else controlled by detecting the loss of exothermia effect of the reaction on the exhaust temperature. In a further modification, the regeneration may take place as described in United States Patent No. 5,406,790 in which the exhaust gas flow is throttled ahead of the absorber and is directed to the absorber through a by-pass.

15 To convert any hydrocarbons that may remain in the exhaust gas, an air injector 13 located downstream of the absorber 1 is activated by the control unit 4 during the fuel injection by the fuel injector 12. In this way, any hydrocarbons still remaining are oxidized to carbon dioxide and water in the downstream catalyst 8.

If desired, the throttle 17 as well as the fuel injector 12 may be omitted, since the
20 fuel injector 7 in the combustion chamber of the engine can enrich the exhaust gas sufficiently.

Since the output of the engine 3 may be reduced during regeneration of the absorbing layer, the system may be arranged so that, when the engine is operating at full power, regeneration may be suppressed at least for a certain length of time.

25 Although the invention has been described herein with reference to specific embodiments, many modifications and variations therein will readily occur to those

skilled in the art. Accordingly, all such variations and modifications are included within the intended scope of the invention.

I CLAIM:

1 1. An internal combustion engine arrangement comprising:
2 a spark-ignited internal combustion engine;
3 an exhaust line receiving exhaust gas from the internal combustion engine;
4 an oxide gas absorber in the exhaust line including a support member; and an
5 absorption layer on a surface of the support member having an enlarged surface area
6 accessible to exhaust gas flowing through the exhaust line for reversible absorption at
7 least one nitrogen oxide (NO_x) and/or at least one oxide of sulfur (SO_x); and,
8 a control unit for controlling the temperature of the absorption layer by adjusting
9 parameters of the exhaust gas so that the absorption layer can be heated to a temperature
10 at which the layer is regenerated by desorbing absorbed NO_x or SO_x.

1 2. An internal combustion engine arrangement according to claim 1 wherein
2 the support member is a metal support member.

1 3. An internal combustion engine arrangement according to claim 2 wherein
2 the metal support member is a metal foil.

1 4. An internal combustion engine arrangement according to claim 2 wherein
2 the metal support member is heatable by application of an electric current.

1 5. An internal combustion engine arrangement according to claim 2 wherein
2 the metal support member has a wall thickness ≤ 0.1 mm.

1 6. An internal combustion engine arrangement according to claim 5 wherein
2 the metal support member has a wall thickness ≤ 0.06 mm.

1 7. An internal combustion engine arrangement according to claim 1 wherein
2 the support member contains a plurality of parallel passages having a closed cross-section
3 through which exhaust gas can be passed and the absorption layer is on the inside surface
4 of the passages.

1 8. An internal combustion engine arrangement according to claim 7 wherein
2 at least some of the passages have a structure causing turbulent gas flow at least over a
3 portion of the passage.

1 9. An internal combustion engine arrangement according to claim 8 wherein
2 the structure causing the turbulent gas flow is at least one of: (a) a variation in cross-
3 section; (b) a corrugation; and (c) a twisting or curvature of the passages.

1 10. An internal combustion engine arrangement according to claim 7 wherein
2 the oxide gas absorber is subdivided into a plurality of segments.

1 11. An internal combustion engine arrangement according to claim 10 wherein
2 the plurality of segments have at least one of: (a) different lengths; (b) different passage
3 cross-sections; (c) different numbers of passages; and (d) spacing between segments of at
4 least 50 cm.

1 12. An internal combustion engine arrangement according to claim 1 wherein
2 the enlarged surface area provides an area of at least 20 m² accessible to the exhaust gas
3 per gram of the absorption layer.

1 13. An internal combustion engine arrangement according to claim 12 wherein
2 the enlarged surface area provides an area of at least 40 m² accessible to the exhaust gas
3 per gram of the absorption layer.

1 14. An internal combustion engine arrangement according to claim 13 wherein
2 the enlarged surface area provides an area of at least 100 m² accessible to the exhaust gas
3 per gram of the absorption layer.

1 15. An internal combustion engine arrangement according to claim 1 wherein
2 the absorption layer contains an aluminum oxide.

1 16. An internal combustion engine arrangement according to claim 15 wherein
2 the absorption layer contains gamma aluminum oxide.

1 17. An internal combustion engine arrangement to claim 1 wherein the
2 absorption layer contains an element selected from the group consisting of alkali metals,
3 alkaline-earth metals, rare earths, lanthanum, titanium, copper and manganese..

1 18. An internal combustion engine arrangement according to claim 1 wherein
2 the absorption layer contains at least one of the elements barium, sodium and potassium.

1 19. An internal combustion engine arrangement according to claim 1 wherein
2 the absorption layer absorbs NO_x and/or SO_x from an exhaust gas with an excess of
3 oxygen during lean operation of the internal combustion engine.

1 20. An internal combustion engine arrangement according to claim 1 wherein
2 the absorption layer releases NO_x and/or SO_x in a reducing atmosphere and/or at low
3 oxygen concentration in the exhaust gas.

1 21. An internal combustion engine arrangement according to either of claim
2 19 or claim 20 including an oxygen concentration determining means for determining a
3 value representing the oxygen concentration in the exhaust gas and supplying a signal
4 representing the oxygen concentration as an input signal to the control unit, and wherein
5 the control unit uses the oxygen concentration signal to control charging or discharging of
6 the absorber.

1 22. An internal combustion engine arrangement according to claim 1 wherein
2 the absorption layer desorbs NO_x and SO_x at an elevated temperature.

1 23. An internal combustion engine arrangement according to claim 22
2 including a temperature determining means for determining a value representing the
3 temperature of at least one of: (a) the exhaust gas; (b) the absorption layer; and
4 (c) the support member; and supplying a signal corresponding to that value as an input
5 signal to the control unit for control of charging or discharging of the absorber.

1 24. An internal combustion engine arrangement according to claim 23
2 wherein the control unit receives signals representing both the oxygen concentration in
3 the exhaust gas and the temperature of the exhaust gas as input signals.

1 25. An internal combustion engine arrangement according to claim 1 wherein
2 the support member is a ceramic member and the absorption layer has a thickness of at
3 least 50 microns.

1 26. An internal combustion engine arrangement according to claim 1 wherein
2 the support member is a metal member and the absorption layer has a thickness of at least
3 25 microns.

4 27. An internal combustion engine arrangement according to claim 1 wherein
5 the absorption layer is applied as a wash coat.

1 28. An internal combustion engine arrangement according to claim 1 wherein
2 the absorption layer contains at least one precious metal.

1 29. An internal combustion engine arrangement according to claim 28 wherein
2 the absorption containing the precious metal constitutes an oxidation catalyst or a three-
3 way catalyst.

1 30. An internal combustion engine arrangement according to claim 1 wherein
2 the absorption layer accessible to the exhaust gas has a pore volume of at least 0.2 cm³/g.

1 31. An internal combustion engine arrangement according to claim 1
2 including an oxidation catalyst separate from the oxide gas absorber.

1 32. An internal combustion engine arrangement according to claim 31 wherein
2 the oxidation catalyst is a three-way catalyst.

1 33. A method for removing at least one nitrogen oxide (NO_x) from the exhaust
2 gas of an internal combustion engine, comprising the steps of:

3 (a) operating an internal combustion engine to produce an exhaust gas flow
4 containing oxygen;

5 (b) passing exhaust gas containing oxygen over an absorber containing an
6 absorbing layer on a surface of a support member;

7 (c) storing the NO_x in the absorbing layer;

8 (d) heating the absorbing layer to a predetermined temperature during the
9 operation of the engine;

10 (e) producing an exhaust gas which is poor in oxygen or an exhaust gas having a
11 stoichiometric excess of a reducing agent;

12 (f) desorbing the NO_x from the absorbing layer and reducing the NO_x in the
13 exhaust gas which is poor in oxygen has a stoichiometric excess of reducing agent while
14 the absorbing layer is a temperature equal to or above the predetermined temperature;

15 (g) again producing an exhaust gas containing oxygen;

16 (h) terminating heating of the absorbing layer to the predetermined temperature;

17 and

18 (j) repeating steps (c) through (h).

1 34. A method according to claim 33 wherein the step of heating the absorbing
2 layer is carried out by at least one of: (a) injecting fuel into the exhaust gas and catalytic
3 combustion thereof, (b) varying the operating conditions of the internal combustion
4 engine, (c) electrical heating of the absorbing layer and (d) using a burner to heat the
5 exhaust gas.

1 35. A method according to claim 33 wherein, before the step of heating the
2 absorbing layer at least to a predetermined temperature during operation of the internal
3 combustion engine, a step of determining whether a temperature value representing the
4 temperature of the absorbing layer is at or above the predetermined temperature is carried
5 out and, if it is determined that the temperature value representing the temperature of the
6 absorbing layer is at or above the predetermined temperature, steps (d) and (b) are
7 omitted.

1 36. A method according to any one of claims 33-35 wherein the support
2 member is a metal support member.

1 37. A method according to any one of claims 33-35 wherein at least one oxide
2 of sulfur (SO_x) is also stored and desorbed by the absorbent layer.

1 38. A method according to any one of claims 33-35 wherein the desorption
2 from the absorber layer is carried out at periodic intervals.

1 39. A method according to any one of claims 33-35 wherein the desorption
2 from the absorbent layer is carried out depending on the amount of gas stored in the
3 absorbent layer.

1 40. A method according to any one of claims 33- 35 wherein the absorbent
2 layer contains gamma-aluminum oxide and at least one element in the group consisting of
3 alkali metals, alkaline-earth metals, rare earths and lanthanum.

1 41. A method according to any one of claims 33-35 wherein the exhaust gas is
2 passed over the absorbent layer with turbulence.

1 42. A method according to any one of claims 33-35 wherein the support
2 member has a plurality of parallel passages..

1 43. A method according to claim 42 wherein the exhaust gas is passed over a
2 plurality of support members containing the gas absorbing layer and having at least one
3 of: (a) different numbers of passages; (b) passages of different flow diameters; and (c)
4 spacings between the support members of at least 50 cm.

1 44. A method according to claim 42 wherein the support member has a
2 plurality of twisted or curved passages.

ABSTRACT OF THE DISCLOSURE

In the embodiments described in the specification, a spark-ignited internal combustion engine has an exhaust line containing an oxide gas absorber for absorbing NO_x and SO_x and desorbing NO_x and SO_x at elevated temperatures. The support member
5 for the oxide gas absorber is a metal foil or a thin walled ceramic support to permit rapid heating and is coated with a layer of a gas absorbing material at least 50 microns thick to permit longer intervals between regeneration, thereby providing effective storage of oxide gases even with fuel consumption-optimized engines.

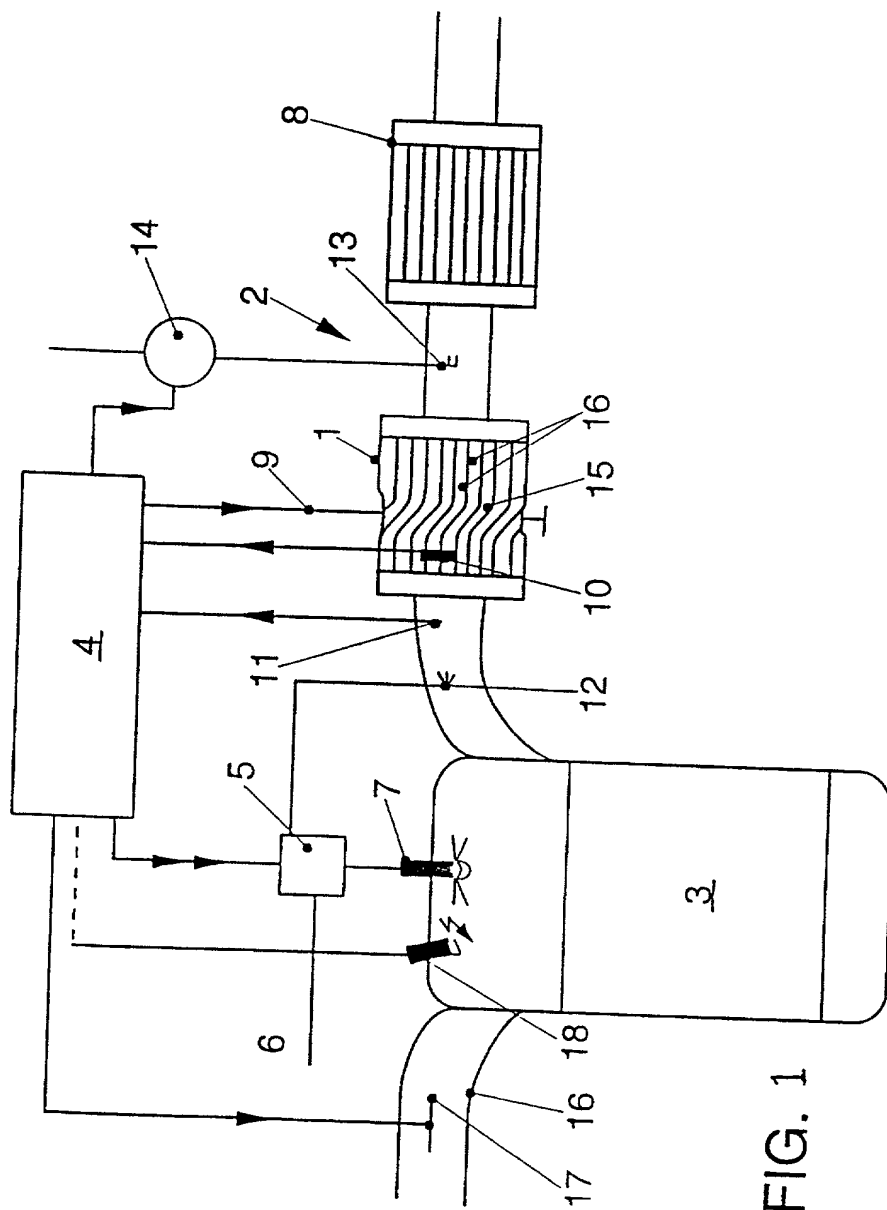


FIG. 1

COMBINED DECLARATION AND POWER OF ATTORNEY

(Original, Design, National Stage of PCT, Divisional, Continuation or C-I-P Application)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SPARK-IGNITED INTENRAL COMBUSTIONENGINE
OXIDE GAS ABSORBING ARRANGEMENT AND METHOD

This declaration is of the following type:

- ☒ original
- ☐ design
- ☐ national stage of PCT.
- ☐ divisional
- ☐ continuation
- ☐ continuation-in-part (C-I-P)

the specification of which:

- (a) ☒ is attached hereto.
- (b) ☐ was filed on as Application Serial No. and was amended on (*if applicable*).
- (c) ☐ was described and claimed in PCT International Application No. filed on and was amended on (*if applicable*).

Acknowledgement of Review of Papers and Duty of Candor

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of the subject matter claimed in this application in accordance with Title 37, Code of Federal Regulations § 1.56.

☐ In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.98.

Priority Claim

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT International Application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT International Application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application on which priority is claimed

- (d) ☐ no such applications have been filed.
- (e) ☒ such applications have been filed as follows:

BAKER & BOTTS, L.L.P.

FILE NO.: A32188 PCT/USA

PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION			
COUNTRY	APPLICATION NO.	DATE OF FILING (day, month, year)	DATE OF ISSUE (day, month, year)
Germany	196 33 049.1	19 August 1996	
			PRIORITY CLAIMED UNDER 35 USC 119
			[X] YES NO []
			[] YES NO []
			[] YES NO []
ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION			
			[] YES NO []
			[] YES NO []
			[] YES NO []

Claim for Benefit of Prior U.S. Provisional Application(s)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

Provisional Application Number	Filing Date

Claim for Benefit of Earlier U.S./PCT Application(s) under 35 U.S.C. 120

(complete this part only if this is a divisional, continuation or C-I-P application)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PCT/EP97/04307

7 August 1997

pending

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status) (patented, pending, abandoned)

Power of Attorney

As a named inventor, I hereby appoint Dana M. Raymond, Reg. No. 18,540; Frederick C. Carver, Reg. No. 17,021; Francis J. Hone, Reg. No. 18,662; Joseph D. Garon, Reg. No. 20,420; Arthur S. Tenser, Reg. No. 18,839; Ronald B. Hildreth, Reg. No. 19,498; Thomas R. Nesbitt, Jr., Reg. No. 22,075; Robert Neuner, Reg. No. 24,316; Richard G. Berkley, Reg. No. 25,465; Richard S. Clark, Reg. No. 26,154; Bradley B. Geist, Reg. No. 27,551; James J. Maune, Reg. No. 26,946; John D. Murnane, Reg. No. 29,836; Henry Tang, Reg. No. 29,705; Robert C. Scheinfeld, Reg. No. 31,300; John A. Fogarty, Jr., Reg. No. 22,348; Louis S. Sorell, Reg. No. 32,439 and Rochelle K. Seide Reg. No. 32,300 of the firm of BAKER & BOTTS, L.L.P., with offices at 30 Rockefeller Plaza, New York, New York 10112, as attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith

SEND CORRESPONDENCE TO: BAKER & BOTTS, L.L.P. 30 ROCKEFELLER PLAZA, NEW YORK, N.Y. 10112 CUSTOMER NUMBER: 21003	DIRECT TELEPHONE CALLS TO: BAKER & BOTTS, L.L.P. (212) 705-5000
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge

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FILE NO.: A32188 PCT/USA

that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF SOLE OR FIRST INVENTOR	LAST NAME Held	FIRST NAME Wolfgang	MIDDLE NAME	
RESIDENCE & CITIZENSHIP	CITY Wolfsburg	STATE or FOREIGN COUNTRY Germany	COUNTRY OF CITIZENSHIP Germany	
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DATE 12/02/99	SIGNATURE OF INVENTOR <i>Wolfgang Held</i>			

Check proper box(es) for any added page(s) forming a part of this declaration

- ☐ Signature for ninth and subsequent joint inventors. Number of pages added _____.
- ☐ Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor.
Number of pages added _____.
- ☐ Signature for inventor who refuses to sign, or cannot be reached, by person authorized under 37 CFR 1.47..
Number of pages added _____.